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Thermally stimulated luminescence mechanism of $Li_6Y(BO_3)_3$:Eu³⁺ single crystals

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Abstract

Thermally stimulated luminescence (TSL) of $\text{Li}_6 Y(\text{BO}_3)_3: \text{Eu}^{3+}$ single crystals has been studied. Radiation-induced absorption of the $\text{Li}_6 Y(\text{BO}_3)_3: \text{Eu}^{3+}$ crystals in the 320–500 nm region has been attributed to the formation of hole oxygen centers. Three peaks on the TSL curve in the T = 325-525 K range has been ascribed to decay of the radiation defects, which occupy non-equivalent crystallographic positions. The activation energy and frequency factor of the main TSL peak at T = 488 K has been determined: E = 1.25 eV, and $s_0 = 1.9 \times 10^{11} \text{ s}^{-1}$, respectively. It has been shown that TSL spectral composition corresponds to Eu^{3+} ions emission. Possible position of localization defects in $\text{Li}_6 Y(\text{BO}_3)_3:\text{Eu}^{3+}$ crystals has been proposed on the base of crystal structure analysis.

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1. Introduction

Nowadays $Li_6RE(BO_3)_3$ (RE = Y, Gd, Eu) single crystals of isostructural orthoborates are being actively studied. In the Li₆RE(BO₃)₃ structure rare earth (RE) polyhedra form chains extended along the [001] direction, and this provides predominantly one-dimensional energy transfer between RE³⁺ ions [1–3]. At present primary data on the luminescent properties of RE³⁺ ions as well as sensitizing of RE³⁺ luminescence with non-RE ions in Li₆RE(BO₃)₃ crystals have been obtained. Luminescent properties of $Li_6RE(BO_3)_3$: Eu^{3+} crystals (RE = Gd, Y) as a red phosphor for plasma display panels were reported in [4,5]. In [6,7] it was shown that $Li_6RE(BO_3)_3:Ce^{3+}$ (RE = Gd, Y) crystals are a promising material for scintillation detectors of thermal neutrons. These crystals contain lithium and boron usually used in inorganic scintillators of thermal neutrons [8]. Nowadays $Li_6Y(BO_3)_3$ (LYBO) doped with RE ions are considered to be promising laser media [9,10]. Utilization of LYBO crystals in laser and scintillation devices implies intense processes of radiation defect formation in material. However,

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radiation-induced defects in this crystal have not been studied sufficiently so far.

Primary thermoluminescent properties of Li₆Gd(BO₃)₃:Eu³⁺ ($Z_{eff.}$ = 46) single crystals have been considered in our recent paper [11]. Complete substitution of gadolinium by yttrium essentially decreases the effective atomic number of LYBO compound ($Z_{eff.}$ = 26), and, consequently, its sensitivity to gamma-background. Studying of radiation induced processes in LYBO:Eu³⁺ isostructural crystal is necessary in view of possible application of material in solid state dosimetry [12]. Thus, the aim of this work is to study radiation defects in LYBO:Eu³⁺ single crystals.

2. Experimental

LYBO:Eu³⁺ single crystals were grown by the Czochralski method according to the procedure [13]. The concentration of europium in grown crystals was determined by atomic emission spectroscopy with arc excitation; the spectrum was registered using a DFS-8 unit. The absorption spectra were recorded using a Specord M40 UV–vis double-beam spectrophotometer. The photoluminescence spectra were obtained by means of a SDL-2 (LOMO) automated complex. The TSL glow curves were recorded using a home-made setup equipped with a FEU-79 PMT at a heating rate of 5 K/min. The samples were irradiated with β -particles (90 Sr/ 90 Y source, with an activity of 1 Ci); with γ -quanta (60 Co source) or with X-quanta (RUP150/300-10-1 X-ray unit, Cu anode; U = 160 kV, I = 9 mA) at room temperature. The LYBO grown crystals were characterized by

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Fig. 1. Absorption spectra of $\text{Li}_6 Y(\text{BO}_3)_3:\text{Eu}^{3+}$ single crystal: (1) before irradiation; (2) after β -irradiation ($D = 10^6$ rad). The inset: differential absorption spectrum of irradiated and non-irradiated $\text{Li}_6 Y(\text{BO}_3)_3:\text{Eu}^{3+}$ crystal.

the following parameters: monoclinic system, $P_{2_1/c}$ space group, a = 7.18192(7), b = 16.4247 (2), c = 6.64193 (5) Å, $\beta = 105.2857$ (7)°, V = 755.77 (0) Å³. The europium concentration in the crystals grown from the Li₆Y_{0.97}Eu_{0.03}(BO₃)₃ initial charge was 0.62 at.% corresponding to the effective segregation coefficient $K_{\rm eff}$ (Eu) of 0.2.

3. Results and discussion

LYBO crystals are transparent in the 176-900 nm range, the band gap being 7.04 eV (56,800 cm⁻¹) [14]. Doping with europium leads to the appearance of a wide charge transfer band (CTB) in the UV, and some narrow lines in the visible region of the spectrum corresponding to the 4f-4f transitions of Eu^{3+} ions (Fig. 1, curve 1). CTB with a maximum at $\lambda = 249$ nm corresponds to the transport of an electron from the oxygen 2p orbital to an unoccupied 4f orbital of europium ion: $Eu^{3+} + O^{2-} \leftrightarrow Eu^{2+} + O^{-}$. The form of the curve between 200 and 250 nm suggests that the stray light limit of spectrophotometer is reached. Thus, the decrease of CTB intensity towards 200 nm might be an artifact connected with spectral sensitivity of the spectrophotometer, and CTB maximum could be placed at slightly higher energy. Nevertheless, position of CTB maximum determined from Fig. 1 is in a good agreement with literature data for LYBO:Eu³⁺ crystal $\lambda = 248.5$ nm [5].

Photoluminescence spectra of LYBO:Eu³⁺ crystals are presented in Fig. 2. LYBO:Eu³⁺ crystal luminescence spectrum consists of the group of lines between 575 and 725 nm, which correspond to the transitions from the first excited level ⁵D₀ to the ⁷F_J (J=0–4) levels of Eu³⁺ ions. The ⁵D₀ \rightarrow ⁷F₂ electric dipole transitions (with a maximum at 613 nm) are predominant. The emission and excitation spectra are found to be in a good agreement with the data from [4,5]. Radioluminescence spectrum of LYBO:Eu³⁺ crystals is similar to the photoluminescence one, thus evidencing the presence of an efficient channel of the energy transfer from matrix to the Eu³⁺ emission centers according to the recombination mechanism.



Fig. 2. Photoluminescence spectra of Li₆Y(BO₃)₃:Eu³⁺ crystal ($\lambda_{ex.}$ = 395 nm): (1) before irradiation; (2) after β -irradiation ($D = 10^6$ rad).

Irradiation of LYBO:Eu³⁺ crystals with β -particles, γ - or X-quanta leads to the decrease of the CTB absorption coefficient, to the appearance of a wide non-elementary band of induced optical absorption in the 320–500 nm range (Fig. 1, curve 2) and to the decrease of the integral photoluminescence intensity of Eu³⁺ ions (Fig. 2, curve 2). After irradiation LYBO:Eu³⁺ samples become yellow. All these processes may be caused by the radiation-induced transition of some part of Eu³⁺ ions into divalent state: Eu³⁺ \rightarrow Eu²⁺. The divalent europium has a larger ionic radius in comparison with the trivalent one ($r_{Eu^{2+}}(6) = 1.31$ Å, $r_{Eu^{3+}}(6) = 1.09$ Å [15]), consequently, the Eu³⁺ \rightarrow Eu²⁺ radiation-induced transition gives rise to relaxation of its oxygen surroundings. The arising excessive charge may be compensated due to local distortion of the borate group or by structural defect in the second coordination.

We assume that the observed radiation-induced coloration of the crystals is connected with the formation of O⁻ hole centers. The O⁻ hole center model in LiB₃O₅ crystals implies the presence of negative charged radiation-induced lithium vacancy in the nearest neighboring [16]. In our opinion, excessive charge of O⁻ center in LYBO:Eu³⁺ crystals is also compensated by lithium vacancy. It may be easily created by impact mechanism taking into account the mobility of lithium ion [17] and the fact that LYBO crystal structure contains a flat network composed of lithium polyhedra, where such a displacement may take place. Moreover, the intrinsic (growth) lithium vacancies arising during the pulling from the melt due to lithium evaporation [18] can act as precursor of radiation-induced defects.

In LYBO:Eu³⁺ crystals boron has only trigonal coordination and occupies three independent positions, therefore the oxygen hole centers in these crystals may be either isolated O⁻ ions (hole is trapped predominantly on one oxygen ion) or BO₃²⁻ ions (hole is uniformly distributed among all the three oxygen atoms) [19]. The valence band top in oxides is usually formed by the 2p oxygen orbitals. So, detaching of the upper states of valence band to the forbidden band is a typical mechanism of the formation of hole centers local levels in oxide crystals [20]. Download English Version:

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